Excimer ultraviolet gas-discharge XeF, XeCl, and KrF lasers

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In all the amino acids with an asymmetric carbon atom the SHG intensity reaches the same level as in lithium formate. Amino acids are known to have wide transparency bands extending to the ultraviolet range right up to 0.2–0.3 μ. Thus, crystals of amino acids and their salts (which are also optically active) may compete with the known materials (phosphates and arsenates of alkali metals, formates, and biphthalates of alkali metals) in the generation of ultraviolet radiation (second harmonic of ruby laser radiation, summation of the second harmonic and fundamental frequency of neodymium laser).

Among noncentrosymmetric crystals there are quite a few organic acids. However, not all of them crystallize easily. Salts of such acids are usually water-soluble, transparent, and have better mechanical properties. Noncentrosymmetric crystals of these salts are additional possible materials with a nonlinear susceptibility. Table I includes four such salts: sodium *p*-nitrophenolate, potassium *L*-aspartate, lithium vanillate, and also the well-known lithium formate monohydrate. Second-harmonic generation is impossible in paranitrophenol, or in vanillic and formic acids because their crystals are centrosymmetric. The range of organic compounds of potential use in nonlinear optics and which can be easily crystallized can be extended by including esters of organic compounds (compounds Nos. 20 and 26, as well as the ethyl *p*-aminobenzoate or Anesthesin—Ref. 2).

An interesting way of producing new nonlinear materials characterized by a high SHG efficiency is the attachment, accompanied by charge transfer, or residues of optically active acids to condensed aromatic systems. Such synthesis gives compounds known in advance to have noncentrosymmetric lattices. Examples of such compounds are Nos. 28 and 29.

We shall conclude by pointing out that investigations of nonlinear properties of organic materials carried out in the Soviet Union and abroad have revealed the existence of a large number of molecular crystals with nonlinear susceptibilities of the order of the susceptibilities of the known alkali niobates (lithium, potassium, and barium–sodium niobates) but grown from solutions. This makes it possible to obtain large optically homogeneous single crystals. The high optical strength (the maximum strength of pure organic materials is not yet known), strong nonlinear susceptibility, ease of preparation of large optical-quality crystals, phase matching, simple synthesis, and low cost are the properties which make it highly desirable to master this new class of materials, which may be found particularly suitable in wide-aperture frequency converters of high-power near-infrared radiation.

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Excimer ultraviolet gas-discharge XeF, XeCl, and KrF lasers

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Gas-discharge XeF, XeCl, and KrF lasers, emitting ultraviolet radiation, were constructed. Stimulated emission from a discharge in XeCl ($\lambda_1 = 3081.6$ Å, $\lambda_2 = 3079.2$ Å) was observed for the first time. The emission spectra of the lasers were determined and a structure was found in the XeF laser spectrum (six lines in the 3487.5–3585.4 Å range). The energy per pulse was 2, 1, and 0.5 mJ and the duration of the laser pulses was 15, 10, and 17 nsec for XeF, XeCl, and KrF lasers, respectively.

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Laser sources continuously tunable in the far ultraviolet are urgently needed in photochemistry and isotope separation and for multistep selective ionization of atoms and ionization and dissociation of molecules. According to recent reports, high-power emission in this range was obtained from lasers utilizing inert-gas halides XeF (Refs. 1 and 2), XeCl (Ref. 3), XeBr (Ref. 4), KrF (Refs. 3 and 5–7), and ArF (Ref. 8); these la-

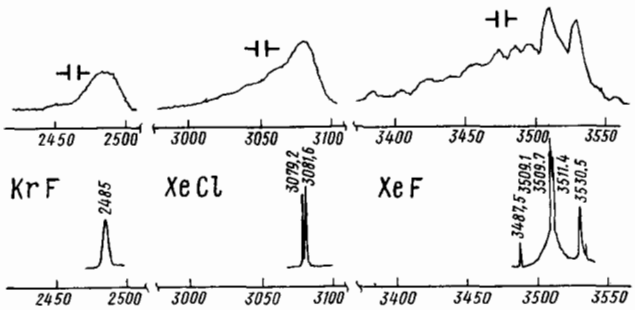

FIG. 1. Spontaneous and stimulated emission spectra of the XeF, XeCl, and KrF molecules.

sers were excited with high-current relativistic-electron beams. One should also mention excimer electric-discharge lasers which have the advantages of compactness and simplicity and yet have a relatively high output power and a comparatively good efficiency in the difficult far ultraviolet range. Stimulated emission from XeF (Refs. 8 and 9) and KrF (Ref. 10) was obtained by electric-discharge excitation.

We built an electric-discharge XeCl laser and found a structure of the emission lines of the XeF laser.

A mixture of gases consisting of He, Xe(Kr), and a halogen donor was excited by a transverse electric discharge by a double Blumlein pulse-shaping line. The donor molecules were NF_3, CF_2Cl_2, C_2F_3Cl, CCl_4, or BCl_3. The main component of the mixture was He. Excited halide molecules appeared as a result of chemical reaction between excited inert-gas atoms and halogen donors. These excited MH* molecules (M is an inert-gas atom and H is a halogen atom) were formed in high vibrational states and were de-excited to lower vibrational levels as a result of collisions with the buffer gas (helium in our experiments). The spontaneous lifetime of the upper electron level ranged from 20 to 50 nsec, depending on the halide. The lower electron level was either weakly bound (in the case of the XeF and XeCl molecules—Refs. 11 and 12, respectively) or repulsive (in the case of KrF).

The excitation system comprised a planar pulse-shaping line of 60×36 cm dimensions and 3.8×10^{-9} F capacitance; it was charged by voltage pulses up to 35 kV. A laser cell was made of glass and its ends were inclined at the Brewster angle. The volume of the active region was $36\times1.1\times0.1\approx4$ cm^3. The resonator was formed by a nontransmitting spherical aluminum mirror ($\rho=5$ m, reflection coefficient $R=85\%$ at $\lambda=337.1$ nm) and a semitransparent plane aluminum mirror. Exit mirrors with reflection coefficients of 70 and 20% and a quartz substrate with reflection coefficient 8% were used. The resonator length was 60 cm.

The spontaneous and stimulated emission spectra were determined with a VMS-1 spectrograph which had a diffraction grating (1200 lines/mm) and a dispersion of 13 Å/mm. The spectra were photographed on Mikrat 200 film.

The energy of laser pulses was measured with a calibrated thermopile and the duration of these pulses was determined with an FÉK-14 coaxial photocell and an I2-7 time-interval meter (the resolution of the recording system was at least 3 nsec).

Figure 1 shows the spontaneous and stimulated emission spectra of the KrF, XeCl, and XeF molecules. The spontaneous emission spectra were obtained for a discharge in the cell without a resonator. The half-width of the spontaneous spectrum of KrF was ~25 Å and that of XeCl was ~30 Å. The spontaneous spectrum of XeF had a strongly truncated structure. The laser spectrum of KrF consisted of a single line at 2485 Å with a half width of ~3.5 Å. The XeCl laser spectrum had two lines in the region of 308 nm and the distance between them was 2.4 Å. The half-widths of these lines were < 0.5 Å. The laser spectrum of XeF consisted of six lines in the region of 350 nm. It was reported in Ref. 9 that the laser spectrum of XeF had three lines with wavelengths 353, 351, and 349 nm. We found that these lines had a structure. The strongest line ($\lambda=351$ nm) consisted of three closely spaced components and the line at $\lambda=353$ nm had two components. The considerable width of the KrF laser line was due to the fact that the laser transition was of the bound–free type.

In Ref. 3 the Cl donor in the XeCl laser was Cl_2. However, Cl_2 absorbed at the stimulated emission wavelength. We used successfully a number of substances which did not absorb in the region of 308 nm: CF_3Cl, C_2F_3Cl, and CCl_4 (Ref. 13), as well as BCl_3. The maximum stimulated emission energy was obtained from the XeCl laser when the composition of the mixture was $He:Xe:CF_2Cl_2=300:8:1$ and the exit mirror had a reflection coefficient $R=20\%$. Stimulated emission was observed only at pressures exceeding 1.2 atm.

Although both CF_2Cl_2 and C_2F_3Cl molecules contained not only chlorine but also fluorine atoms, stimulated emission was observed only at the wavelength of 308 nm. This was due to the fact that the energy of the C–F bonds (116 kcal/mole) was higher than the energy of the C–Cl bonds (81 kcal/mole) and because the reaction of excited xenon atoms with CF_2Cl_2 and C_2F_3Cl produced the XeCl* molecules.

In the XeF laser we used a mixture of gases whose composition was $He:Xe:NF_3=220:3.5:1$. The maximum energy was obtained when the substrate of the exit

TABLE I. Parameters of laser pulses and characteristics of active media.

Molecule	Lasing wavelength, Å	Energy per pulse, mJ	Pulse duration, nsec	Pressure in active medium, atm	Halogen donors
XeF	3535.4 3530.5 3511.4 3509.7 3509.1 3487.5	2	15	0.7	NF_3
XeCl	3081.6 3079.2	1	10	2.0	CF_2Cl_2, CCl_4, BCl_3, C_2F_3Cl
KrF	2485	0.5	17	1.2	NF_3

mirror had a reflection coefficient of 8%. When NF_3 was replaced with SF_6, stimulated emission was again obtained but the output energy was lower.

In the KrF laser we used a mixture of gases of the composition He : Kr : NF_3 = 500 : 50 : 1. Stimulated emission appeared when the total pressure exceeded 0.5 atm and only when a mirror with $R = 70\%$ was used.

Table I gives the parameters of the laser pulses and active media. The divergence of the laser radiation was $\sim 10^{-2}$ rad in the direction corresponding to the larger transverse dimension of the laser cell and $\sim 10^{-3}$ rad in the perpendicular direction.

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A possible way of increasing the precision of comparison of the values of the Planck constant in a certain frequency range

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A proposal is made for an experiment in which nonlinear optics and laser spectroscopy methods are used to increase by several orders of magnitude the precision of a quantitative criterion characterizing the absence of a frequency dispersion of the Planck constant.

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The currently accepted value of the Planck constant, $h = 6.626176 \times 10^{-27}$ erg·sec, is known with an error of $\delta_0 = 5.4 \times 10^{-6}$ (Ref. 1). The Planck constant h does not exhibit frequency dispersion, i.e.,

$$dh/d\nu = 0 \qquad (1)$$

in the sense that the coefficient of proportionality relating the energy of a quantum transition $E = h\nu$ to the frequency ν of an absorbed or emitted photon is independent of ν. This statement, which is one of the cornerstones of post-classical physics, can be represented quantitatively by the precision

$$\delta = (\bar{\nu}/h)(dh/d\nu), \qquad (2)$$

with which it is found experimentally that Eq. (1) is satisfied (here, $\bar{\nu}$ is the average frequency). Apart from direct measurement of δ, we can also estimate it indirectly and approximately from the ratio of the error δ_0 in the determination of the absolute value of h and the frequency interval in which the constant is measured, and this procedure gives a rough estimate $\delta \approx 10^{-6}$. A negative feature of this procedure is the physicomethodological difference between the methods of measurement of h at the points in the frequency interval where the comparison is being made if this interval is sufficiently wide.

Nonlinear optics and Doppler-broadening-free laser spectroscopy[2] methods make it possible to obtain an upper limit of δ by a direct and methodologically unified experiment.

Radiation of a highly monochromatic laser with a tunable frequency ν_0 and a line width $\Delta\nu_0$ is split into two beams, the first of which excites (in a nonlinear frequency multiplier) a K-th harmonic of frequency $\nu_1 = K\nu_0$ ($K = 2, 4, 6, \ldots$) and the second beam is frequency-shifted within a narrow range to $\nu_2 = \nu_0 + \Delta\nu$ $\times (|\Delta\nu| \ll \nu_0)$ by, for example, reflection from a turning prism which is moving linearly at a velocity $v = (c/2) \times (\Delta\nu/\nu_0)$ (c is the velocity of light). The shift $\Delta\nu$ is selected by a quadratic-law photodetector and is measured as a difference frequency $\nu_2 - \nu_0$ in the rf range.